

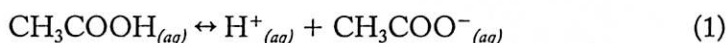
Determination of Acid Ionization Constant of a Weak Acid

PURPOSE

- Calculate the K_a of a weak monoprotic acid, given its pH and initial concentration
- Calculate the K_a of a weak monoprotic acid from pH of a solution of known amounts of acetic acid and sodium acetate
- Determine the K_a of a monoprotic or diprotic acid from a titration curve, using various analytic methods

INTRODUCTION

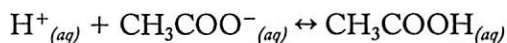
Weak acids are weak electrolytes, meaning that the molecular monoprotic acid acetic (ethanoic) acid, CH_3COOH , ionizes to a small extent in an aqueous solution, forming a proton (H^+) and CH_3COO^- , the conjugate base of CH_3COOH .



$$\text{Equilibrium constant } (K_a) = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

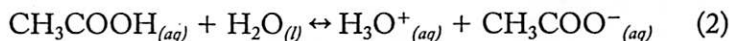
As this is an equilibrium reaction, the relative strength of the acid may be thought of as the extent to which the acid ionizes, because the more an acid ionizes, the larger the **equilibrium constant**, or K_a , value.

Applying the Bronsted-Lowry definition of a base (as "a proton acceptor") makes determining the conjugate base easier. The **conjugate base** is the species that accepts the proton in the reverse reaction; that is,



Another way to think of the conjugate base is as the species evolving from the acid after a proton has been donated (conjugate base = Acid - H^+). By either approach you choose, CH_3COO^- accepts a proton in the reverse reaction, so it is the conjugate base of CH_3COOH .

Some authorities show reaction (1) as a hydrolysis reaction with the acid donating a proton to water, forming the hydronium ion (H_3O^+) and the conjugate base of the acid. So the generic monoprotic acid hydrolysis reaction is



$$\text{Equilibrium constant } (K_a) = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

In this reaction, because it accepts a proton in the reverse reaction, CH_3COO^- is once again the conjugate base of CH_3COOH . You can think of the hydronium ion as a hydrated proton and the conjugate acid of water, which is the base in the forward reaction. These reactions really are interchangeable.

The expression for pH in reaction (1) is

$$\text{pH} = -\log[\text{H}^+]$$

The expression for pH for reaction (2) would not include the proton; rather, it must include the hydronium ion concentration instead:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

How does one determine the **ionization constant** (K_a) of an acid? By reviewing the equilibrium constant expression for acetic acid

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

it is clear that one must determine the concentrations of H^+ , CH_3COO^- , and CH_3COOH once equilibrium is established. Simply measuring the pH of an acetic acid solution, to verify that the pH is constant, is one way to conclude that equilibrium is established, because this shows that there is no net change in $[\text{H}^+]$.

Pre-Lab Preparation To gain a helpful mindset for understanding the necessary measurements for this lab, think how to go about calculating the solution to this problem:

What is the pH of 0.10 M acetic acid, given that the K_a of the acid is 1.8×10^{-5} at 298 K?

Many sources use tables to show such calculations. As an example, the partial table below accounts for the initial concentrations in mol/L of the species (given as **I**), the change in concentrations needed to reach equilibrium (given as **C**), and finally, the equilibrium concentrations of all species (given as **E**).

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

		$\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow$	$\text{H}^+_{(aq)}$	$+ \text{CH}_3\text{COO}^-_{(aq)}$
Initial concentration (M)	I	0.10	0	0
Change in concentration (M)	C			
Equilibrium concentration (M)	E			

This approach starts initially with the weak acid unionized, an assumption that dictates that the initial concentration of the products must be zero, because none of the acid has dissociated to form the products. To reach equilibrium, the acid must dissociate, so the change in its concentration must decrease, or be negative (–), while the change in concentrations of the products must increase, or be positive (+), as shown now in the **C** line of the table.

		$\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow$	$\text{H}^+_{(aq)}$	$+ \text{CH}_3\text{COO}^-_{(aq)}$
Initial concentration (M)	I	0.10	0	0
Change in concentration (M)	C	–	+	+
Equilibrium concentration (M)	E			

The reaction stoichiometry must be used to determine the magnitude of the change. In the case of acetic acid, the mole ratio of acetic acid to proton to acetate is 1 : 1 : 1. This gives only the relative change in concentration, but we can define the variable x as “the change in concentration of acetic acid.” Then, using the 1 : 1 : 1 stoichiometric mole ratio, we can rewrite the **C** line in the table, as follows:

		$\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow$	$\text{H}^+_{(aq)}$	$+ \text{CH}_3\text{COO}^-_{(aq)}$
Initial concentration (M)	I	0.10	0	0
Change in concentration (M)	C	$-x$	$+x$	$+x$
Equilibrium concentration (M)	E			

Because $E = I + C$, you can determine the equilibrium concentration by simply adding the **I** line to the **C** line:

		$\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow$	$\text{H}^+_{(aq)}$	$+ \text{CH}_3\text{COO}^-_{(aq)}$
Initial concentration (M)	I	0.10	0	0
Change in concentration (M)	C	$-x$	$+x$	$+x$
Equilibrium concentration (M)	E	$0.10 - x$	$+x$	$+x$

Substituting the **E** line into the equilibrium constant expression yields the following:

$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.10 - x]}$$

At this point, there is a “fork in the road.” Because the magnitude of the K_a is very small compared to the magnitude of the initial concentration of the acetic acid—more than 5,000 times smaller—we recognize that the amount of acetic acid x that ionizes will likely be much smaller than the initial concentration. So when x is subtracted from 0.10, it is unlikely that the value of 0.10 will change, once the difference is represented to the correct number of significant figures. So, it is reasonable to *assume* that $x \ll 0.10$. Doing so allows us to simplify the expression $0.10 - x$ to 0.10. Then the equilibrium equation becomes

$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.10]}$$

which can be solved for x , without using the quadratic formula, to give 0.0013 *M*. Substituting this x value back into the table, we have

		$\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow$	$\text{H}^+_{(aq)}$	$+ \text{CH}_3\text{COO}^-_{(aq)}$
Initial concentration (M)	I	0.10	0	0
Change in concentration (M)	C	-0.0013	$+0.0013$	$+0.0013$
Equilibrium concentration (M)	E	$0.10 - 0.0013$	0.0013	0.0013

As we assumed, the expression $0.10 - 0.0013$ is equivalent to 0.10, once the rules of significant figures are applied. Although $0.10 - 0.0013 = 0.0987$, the rules for significant figures dictate that the difference be reported to 2 decimal places. Thus 0.0987 must be rounded to 0.10, and the assumption that $x \ll 0.10$, so that $0.10 - x = 0.10$, is shown to be valid. This assumption can also be checked by solving the original quadratic equation for the equilibrium constant:

$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.10 - x]}$$

There are a number of ways to solve for the constant. First, many modern calculators have SOLVER functions that can be used to solve this quadratic. Alternatively, one can resort to the old standby, pencil-on-paper method of the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

To solve for x , we rearrange our quadratic to

$$0 = x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-6}$$

and substitute into the formula the coefficients:

$$a = 1 \qquad b = 1.8 \times 10^{-5} \qquad c = -1.8 \times 10^{-6}$$

Bear in mind that although there are two roots to any quadratic, only one is a possible answer for this problem. If the root is negative, it can easily be ruled out because negative x is not possible in an equilibrium problem. (Note: the “-” in “- x ” that appears in the ICE table indicates a decrease in concentration, not a negative value for x .) Also, because x represents the equilibrium concentration of H^+ and CH_3COO^- , it cannot be a negative number. Moreover, if a root of the quadratic equation were substituted back into the table and the subtraction yielded a negative concentration at equilibrium, this would be an impossible situation.

And finally, the roots of the quadratic can also be found by graphing the quadratic equation. Here are instructions for using a generic Texas Instruments graphing calculator:

1. Turn on your calculator by pressing the “ON” button in the bottom left corner.
2. Press the “Y=” button in the upper left-hand corner.
3. Set the equation equal to zero.
 - i. You must subtract $1.8E-5$ from both sides of the equation so that it reads $0 = \{(x)(x) / (0.10 - x)\} - 1.8E-5$.
 - ii. You can then plug this equation into your calculator.
4. Then in “Y2,” set the equation equal to zero.
5. Press the ZOOM button, the middle button on the top line, and scroll down to “6:ZStandard” and press ENTER.
6. Next press the TRACE button, the second-to-last button in the top right of the calculator.
7. Now press the “2nd” button, below the “Y=” button, and then press the CALC button (this button is the same as the GRAPH button, but now uses its second function).
8. Scroll down to “5:Intersect” and press ENTER.
9. The graph screen will come up again with the equation and the questions “First curve?” Press ENTER twice (you are selecting both graphs) and then you must scroll with the arrow keys right or left to make a guess at where your graph crosses the x -axis. Then press ENTER.
10. In the bottom left corner of the screen you will see “X= ___.” This is one of your x values.
11. To find the other x value, repeat Steps 7–9, but this time use the other intersection point.
12. You now have two values for x that can satisfy the equation. However, only one of these numbers is a plausible answer (the value should be positive and a relatively small number, close to 0.0013).

At this point, the pH of the solution can be calculated. Because, at equilibrium, $[H^+] = 0.0013 M$, then

$$pH = -\log[0.0013] = 2.88$$

According to rules for significant figure for pH values (or pANYTHING values), the numbers to the right of the decimal point are significant. Because the pH will have two decimal places, 2.88 is the correct pH value.

Procedure Preview In our analysis of the problem to this point, the K_a and initial concentration of the acid were used to determine the pH of the solution. Now suppose the problem were reframed; for example:

How can you calculate the K_a of a weak monoprotic acid given that the pH of a 0.10 M solution is 2.88?

Could the problem be worked backwards? Certainly, and you are now in a position to begin your lab experimentation with equilibrium reactions of weak acids. Speak with your instructor about which of the three methods presented in the following pages you are to carry out.

Method I: Determining K_a of a Weak Acid by Using pH and Concentration of Acid

To determine the K_a of an acid, all one needs is the pH of the solution and the concentration of the acid. Measuring the pH requires a calibrated pH probe. By reviewing Experiment 8 of this lab manual, in which the mass percent of acetic acid in vinegar was found, you will recall that the concentration of an acid can be determined by titrating a known volume of acid solution, using a standardized base and phenolphthalein as the indicator. Then, looking at the calculation tables, the pH can be used to calculate the equilibrium concentration of H^+ and acetate ion. The titration data can be used to calculate the initial concentration of acetic acid.

		$CH_3COOH_{(aq)} \leftrightarrow$	$H^+_{(aq)}$	$+ CH_3COO^-_{(aq)}$
Initial concentration (M) I		y	0	0
Change in concentration (M) C		$-x$	$+x$	$+x$
Equilibrium concentration (M) E		$y - x$	$+x$	$+x$

Now, all that separates the K_a value from you is the substitution of your values into the equilibrium constant expression and making the calculations.

MATERIALS

- ethanoic (acetic) acid solution
- standardized NaOH solution
- phenolphthalein
- buret
- measuring device for 10.00 mL (pipet, buret, or graduated cylinder)
- calibrated pH probe
- beaker
- microstir bar (see Appendix C)
- magnetic stir plate
- distilled water (in squirt bottle)

PROCEDURE

In this procedure you will find the concentration of ions in solution to determine K_a given initial pH.

Step A Prepare the buret by rinsing it with standardized NaOH; remove any air bubbles from tip of buret.

Step B Record initial volume of NaOH in your data table.

Step C Record actual concentration of NaOH solution in your data table.

Step D Measure pH of acetic acid sample.

Step E Transfer 10.00 mL of the acetic acid sample to a beaker, using a measuring device determined by your instructor. Record the exact volume of acid that you added.

Step F Add 2 drops of phenolphthalein to solution and a microstir bar to beaker.

Step G Place beaker on the magnetic stir plate.

Step H Titrate the acid sample by adding NaOH solution until a faint pink color is permanent. You must be patient close to the endpoint, because it takes a few seconds for complete mixing of the solution and the color change of indicator.

Step I Record the final volume of NaOH.

Step J Repeat Steps A–I, if directed by your instructor.

Calculations (Method I)

1. Calculate the number of moles of NaOH that were needed to neutralize the acetic acid sample.
2. Using the volume of acid you titrated, calculate the concentration of the acetic acid sample.
3. Using the pH of the acetic acid sample, calculate the equilibrium concentration of H^+ .
4. Using your answer to Question 3, calculate the equilibrium concentrations of the acetate ion and acetic acid.
5. Using your answers to Questions 3 and 4, calculate the K_a for acetic acid.
6. Repeat for a second sample, if applicable.
7. Compare your calculated K_a with the actual K_a of acetic acid.
8. Propose one possible error that could have resulted in a calculated K_a that is too great. Explain how this error would have resulted.

Method II: Determining K_a from pH of Solution Made from Known Amounts of Acid and Conjugate Base

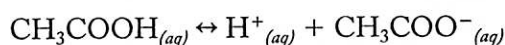
This method will take advantage of an important fact of acid equilibrium highlighted by the following problem:

How can you calculate the pH of a solution made when 25.0 mL of 0.10 M acetic acid is mixed with 50.0 mL of 0.050 M sodium acetate? (K_a acetic acid = 1.8×10^{-5} . Assume volumes are additive.)

First, it is important to address the solution of sodium acetate to determine that

- it is a strong electrolyte, so the sodium acetate ionizes 100%;
- the acetate ion is the conjugate base of acetic acid.

Thus, when these two solutions are mixed, there is no chemical reaction, but rather a solution containing a weak acid and the salt of its conjugate base. The resulting solution can still be described by the following equilibrium:



In order to address this equilibrium, we must determine the initial concentrations of all species after the two solutions are mixed.

$$[\text{CH}_3\text{COOH}]_{\text{initial}} = \frac{0.10 \text{ moles CH}_3\text{COOH}}{1.00 \text{ L}} \left| \frac{25.0 \text{ mL}}{(25.0 \text{ mL} + 50.0 \text{ mL})} \right| = 0.033 \text{ M}$$

$$[\text{CH}_3\text{COO}^-]_{\text{initial}} = \frac{0.050 \text{ moles NaCH}_3\text{COO}}{1.00 \text{ L}} \left| \frac{50.0 \text{ mL}}{(50.0 \text{ mL} + 25.0 \text{ mL})} \right| = 0.033 \text{ M}$$

Now, back to the equilibrium. It is vital to note that *initially* both the acid and its conjugate base are present:

	$\text{CH}_3\text{COOH}_{(aq)} \leftrightarrow$	$\text{H}^+_{(aq)}$	$+ \text{CH}_3\text{COO}^-_{(aq)}$
Initial concentration (M) I	0.33	0	0.33
Change in concentration (M) C	$-x$	$+x$	$+x$
Equilibrium concentration (M) E	$0.33 - x$	$+x$	$0.33 + x$

Because the acid has not ionized initially, no protons are present and, therefore, some must be formed as the reaction shifts to achieve equilibrium.

$$1.8 \times 10^{-5} = \frac{[x][0.33 + x]}{[0.33 - x]}$$

Because the conjugate is present to start, less of the acid has to ionize to get the reaction quotient, Q , to equal K and achieve equilibrium. So based on the ideas discussed earlier in the introductory problem, let us *assume* $x \ll 0.33$, so that the addition of x to 0.33 or the subtraction of x from 0.33 will not, to significant figures, alter this value; in other words, $0.33 - x = 0.33$ and also $0.33 + x = 0.33$. (As before, check that your assumptions are valid. To significant figures:

$$0.33 + 0.000018 = 0.33 \text{ and } 0.33 - 0.000018 = 0.33$$

It is left as an exercise for you to conduct a second check, by solving the quadratic equation by some method, to confirm the validity of the assumptions.)

Now the equilibrium is simplified to:

$$1.8 \times 10^{-5} = \frac{[x][0.33]}{[0.33]}$$

and, because 0.33 divided by itself is 1,

$$1.8 \times 10^{-5} = x = [\text{H}^+] \text{ and}$$

$$\text{pH} = -\log[1.8 \times 10^{-5}] = 4.74$$

Moreover, because

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

when $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = [\text{H}^+]$$

Take note of this very special relationship: when the equilibrium concentration of an acid equals the concentration of its conjugate base,

$$[\text{H}^+] = K_a \text{ and } -\log[\text{H}^+] = -\log K_a \\ \text{so, pH} = \text{p}K_a$$

When the equilibrium relationship is rearranged as follows

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{or} \quad \frac{K_a}{[\text{H}^+]} = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

and the $-\log$ of the two sides are taken, then

$$\text{p}K_a - \text{pH} = -\log \left\{ \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right\}$$

which can be restated algebraically as

$$\text{pH} = \text{p}K_a + \log \left\{ \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right\}$$

which is the **Henderson-Hasselbalch equation**.

In brief, by making a solution that has equal concentrations (therefore, equal moles) of acid and conjugate base, and taking the pH of this solution, the $\text{p}K_a$ of the acid will also be measured. Then the K_a can be calculated using

$$10^{-\text{p}K_a} = K_a$$

It is important to note that, because K_a is constant at a given temperature, it is the ratio of concentrations of conjugate base to weak acid that determines the $[\text{H}^+]$ and, as a result, the pH.

MATERIALS

- acetic acid solution
- standardized NaOH solution
- phenolphthalein
- buret
- measuring device for 25.00 mL (pipet, buret, or graduated cylinder)
- calibrated pH probe
- beaker
- microstir bar (*see Appendix C*)
- magnetic stir plate
- distilled water (in squirt bottle)

PROCEDURE

In this procedure you will first determine the concentrations of acetic acid and sodium acetate in solution in order to calculate K_a .

Step A Prepare the buret by rinsing it with standardized NaOH; remove any air bubbles from the tip.

Step B Record the initial volume of NaOH in your data table.

Step C Record the actual concentration of NaOH solution.

Step D Transfer 25.00 mL of acetic acid sample to a beaker, using a measuring device chosen by your instructor. Record the exact volume of acid added.

Step E Add 2 drops of phenolphthalein to solution and the microstir bar to beaker.

Step F Place the beaker on the magnetic stir plate.

Step G Titrate the acid sample by adding NaOH solution until faint pink color is permanent. Be patient close to the endpoint, because it takes a few seconds for complete mixing of the solution and color change of indicator.

Step H Record the final volume of NaOH.

Step I Label beaker with this sample and keep sample.

- Step J** Measure a second sample of acetic acid that is exactly the same volume as the sample you titrated. See Step D for the exact volume used in first sample.
- Step K** Pour this sample, measured in Step J, into the beaker containing the titrated sample of acetic saved in Step I. Stir thoroughly.
- Step L** Rinse the pH meter tip with distilled water and pat dry with paper towel.
- Step M** Place cleaned pH probe in sample and allow pH reading to stabilize while solution is being stirred (manually or by using stir bar and magnetic stirrer). Record the pH of this solution.
- Step N** Dilute this sample by adding 10.0 mL of distilled water and mix thoroughly.
- Step O** Rinse the pH meter tip with distilled water and pat dry with paper towel.
- Step P** Place the cleaned pH probe in the sample and allow pH reading to stabilize while the solution is being stirred (manually or with stir bar and magnetic stirrer). Record the pH of this solution.

Calculations (Method II)

1. Write a balanced chemical reaction equation for the titration reaction between acetic acid and sodium hydroxide.
2. Calculate the number of moles of NaOH needed to neutralize the acetic acid sample.
3. Calculate the number of moles of acetic acid in your sample.
4. Calculate the moles of sodium acetate that were formed during the titration.
5. Compare the number of moles of acetic acid and sodium acetate present in the solution you made during Step K.
6. Assuming that volumes are additive, calculate the concentrations of acetic acid and sodium acetate in the solution made during Step K.
7. Using the pH from Step M and the answer to Question 6, calculate K_a for acetic acid.
8. Compare your calculated K_a with the actual K_a of acetic acid.
9. Compare the pH reading taken in Step M with that taken in Step P.
10. Did you expect the pH to change much when the sample was diluted? Explain why or why not. Be sure to show quantitative calculations to support your answer.

Post-Lab Questions

Did you need to know:

1. Exact volume of acid or base? Explain.
2. Initial concentration of the base? Explain.
3. Initial pH of the acid or base? Explain.
4. Final pH of the acid after the titration? Explain.
5. Final pH of the mixture from Step K? Explain.